

# A Membrane Reactor for H<sub>2</sub>S Decomposition\*

D. Edlund (Bendresearch@bendres.com; 541-382-4100)

Bend Research, Inc.  
64550 Research Road  
Bend, OR 97701-8599

## Introduction

Hydrogen sulfide (H<sub>2</sub>S) is a common contaminant produced during gasification of coal and refining petroleum and is often present in natural gas. Federal and state regulations limit the discharge of H<sub>2</sub>S to the atmosphere, and commercial methods exist for removal of H<sub>2</sub>S, but they have drawbacks. Generally, these methods produce other pollutants (e.g., sulfur oxides) or hazardous wastes (e.g., metal sulfides). Clearly, new methods are needed for the disposal of H<sub>2</sub>S in an environmentally benign fashion.

It has long been recognized that H<sub>2</sub>S can be thermally decomposed, yielding hydrogen and elemental sulfur (S<sub>2</sub>) as the primary byproducts (Raymont, 1975). However, the equilibrium constant for this thermolysis reaction is unfavorable. The reaction must be conducted at about 700°C to achieve even 10% conversion to hydrogen and sulfur, and complete decomposition of H<sub>2</sub>S is achieved only at temperatures above 1500°C.

Given the high reaction temperatures and unfavorable equilibrium constant, it is not practical to achieve complete decomposition of H<sub>2</sub>S by condensing or otherwise removing the byproduct sulfur and, to date, selective removal of the byproduct hydrogen has not been a practical alternative. Ceramic membranes, which can tolerate the high reaction temperatures, are not sufficiently selective for hydrogen. Metallic membranes do have high selectivity for hydrogen and tolerate high operating temperatures but, to date, have not been compatible with H<sub>2</sub>S. In this paper, we describe our research to develop a practical metal-membrane-based system for the direct thermolysis of H<sub>2</sub>S.

## Objectives

The objectives of this work were to develop practical and economical solutions to key technical problems that have limited the suitability of metal-membrane reactors for direct thermolysis of H<sub>2</sub>S. Specifically, the objectives of this work were to

1. demonstrate high hydrogen flux through a sulfidation-resistant metal membrane;

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2. identify structural alloys or coatings for use in fabricating membrane modules that are resistant to corrosion by hot  $\text{H}_2\text{S}$ ;
3. develop membrane-module designs that are efficient and economical; and
4. achieve these objectives within the overall economic constraints (e.g., capital costs, membrane lifetimes) dictated by the specific application.

## Technical Approach

Our technical approach is to use a metal-membrane reactor to achieve direct thermolysis of  $\text{H}_2\text{S}$  at high temperatures. In this new process, hot gas from the coal gasifier, rich in  $\text{H}_2\text{S}$  but depleted of  $\text{H}_2$ , is fed to the metal-membrane reactor at  $\geq 500^\circ\text{C}$  (see Figure 1). At these high temperatures, the thermal decomposition of  $\text{H}_2\text{S}$  over a catalyst is a very fast reaction (Edlund and Pledger, 1993). However, as noted above, at equilibrium, the reaction proceeds to only 10% to 20% completion (producing  $\text{H}_2$  and  $\text{S}_2$  predominantly) due to limitations imposed by the thermodynamic equilibrium. In our process, as  $\text{H}_2$  is produced within the metal-membrane reactor (Figure 2), it is selectively and rapidly separated from the hot feed gases by an  $\text{H}_2$ -permeable metal membrane, causing the  $\text{H}_2\text{S}$  decomposition reaction to be driven toward completion. The membrane reactor, then, decomposes  $\text{H}_2\text{S}$  almost completely, producing only  $\text{H}_2$  and  $\text{S}_2$  as byproducts. Unlike conventional  $\text{H}_2\text{S}$ -removal technologies (e.g., the Claus process), the process does not produce sulfur oxides or other environmentally objectionable byproducts.

The  $\text{H}_2$  that permeates the metal membrane is catalytically reacted with oxygen to form water or is removed by a sweep stream. (If the sweep gas is condensable [e.g., steam], then pure  $\text{H}_2$  may be recovered at moderate pressures.) However, burning the permeate  $\text{H}_2$  is probably preferred for applications in which  $\text{H}_2\text{S}$  is a minor component of the feed stream (as in coal gasification), because

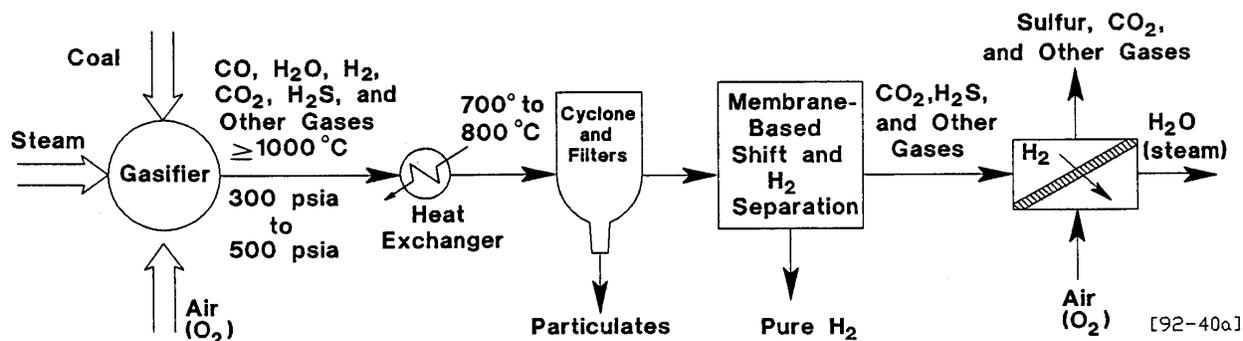


Figure 1. Membrane-Reactor Process for Efficiently Separating and Decomposing  $\text{H}_2\text{S}$  From a Hot Coal-Gas Stream. (The membrane-based shift and  $\text{H}_2$ -separation process has been developed under a separate DOE program [Grant No. DE-FG03-91ER81229].)

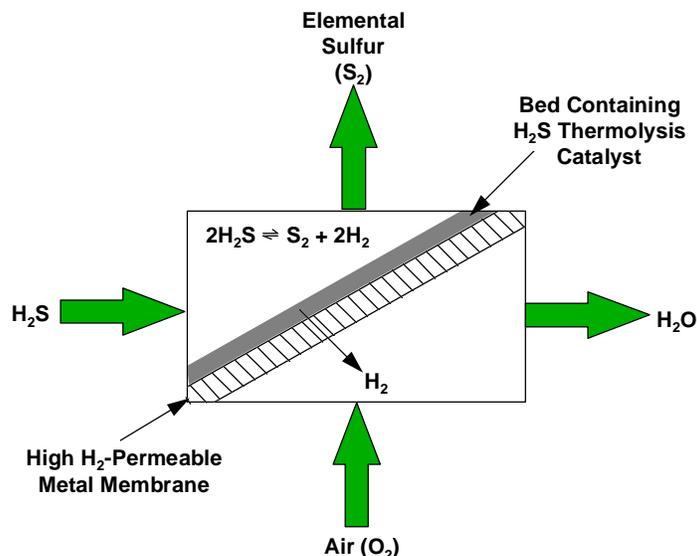
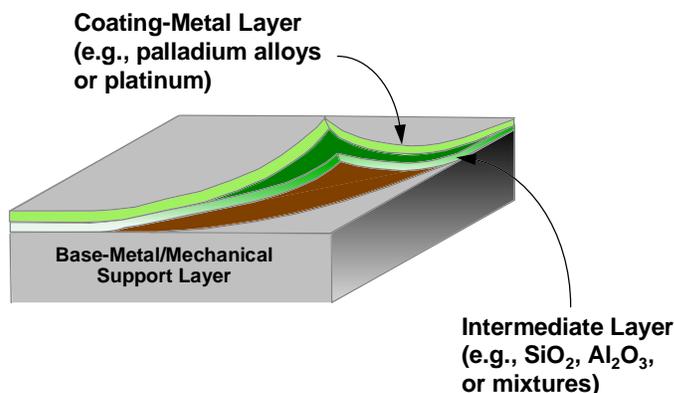


Figure 2. Membrane-Reactor Process to Drive the Thermal Decomposition of  $\text{H}_2\text{S}$  Toward Completion

- the energy produced by burning the permeate  $\text{H}_2$  more than compensates for the energy consumed by the endothermic  $\text{H}_2\text{S}$  decomposition reaction; and
- a low partial pressure of  $\text{H}_2$  is maintained at the permeate side of the membrane as a result of the reaction, thereby providing a high driving force for  $\text{H}_2$  permeation.

The process is based on the use of a composite-metal membrane that we have developed. As shown in Figure 3, the membrane consists of three distinct layers: (1) a base-metal/mechanical support layer, (2) an intermediate layer, and (3) a coating-metal layer, as shown in Figure 3. If the total sulfur concentration of the feed stream is high ( $\geq 5$  ppm), the coating-metal layer must be an  $\text{H}_2$ -permeable metal that is resistant to chemical corrosion by  $\text{H}_2\text{S}$  (e.g., Pd alloyed with about 40% Cu—see below).



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Figure 3. Key Features of Bend Research Composite-Metal Membrane

In a parallel DOE program, we demonstrated that this composite-metal membrane effectively drives the water-gas shift (WGS) reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$ ) toward complete conversion at high temperature by removing  $\text{H}_2$  as it is produced (Edlund et al., 1995). This result shows the promise of the composite-metal membrane for use in a multi-stage membrane-reactor process to maximize the production of pure  $\text{H}_2$  during coal gasification, as well as to decompose the  $\text{H}_2\text{S}$  present in the feed stream.

## Project Description

This program consisted of experimental evaluation of new metal-membrane compositions, experimental evaluation of the corrosion resistance of structural alloys and coatings for use in fabricating membrane reactors, development and evaluation of new membrane reactor designs, and economic analysis of the membrane reactor-based process for  $\text{H}_2\text{S}$  thermolysis and membrane-reactor fabrication. Our results are described below.

## Results

### Evaluation Of New Metal Membrane Compositions

Alloys of Au with Pd are known to exhibit  $\text{H}_2$  permeability in the presence of low concentrations (<20 ppm) of  $\text{H}_2\text{S}$  at about 300°C (McKinley, 1967). Surprisingly, McKinley also reports that Pd-Cu alloys are more resistant than Pd-Ag alloys or pure Pd to  $\text{H}_2\text{S}$  (McKinley, 1967). Reasoning that the  $\text{H}_2$  permeability of these sulfur-resistant alloys should increase with increasing operating temperature and that they should exhibit even greater tolerance to  $\text{H}_2\text{S}$  at elevated operating temperatures, we evaluated Au-coated Pd and Pd-Cu alloys for  $\text{H}_2$  flux in the presence of 50 ppm to 10% at 500°C (the minimum temperature that is practical for  $\text{H}_2\text{S}$  thermolysis). Because the Pd-Au alloys did not perform as well as the Pd-Cu alloy, the remainder of this paper is focused on Pd-Cu membranes.

We purchased an alloy of Pd with 40 wt% Cu (Pd-40Cu) as foil of two different thicknesses (nominally 25  $\mu\text{m}$  and 50  $\mu\text{m}$  thick) and tested it for resistance to  $\text{H}_2\text{S}$ . Figure 4 shows data for long-term stability tests of the 50- $\mu\text{m}$ -thick Pd-40Cu membrane. As the figure shows, the Pd-40Cu membrane retained relatively high flux in the presence of high  $\text{H}_2\text{S}$  concentrations.

Furthermore, the Pd-40Cu alloy is not permanently poisoned by exposure to 10%  $\text{H}_2\text{S}$  and the membrane exhibited stable flux over 350 hours (14 days) of continuous operation (the duration of the experiment, see Figure 4). In addition to demonstrating exceptional resistance to  $\text{H}_2\text{S}$  at operating temperatures  $\geq 500^\circ\text{C}$  in the laboratory, the Pd-40Cu composite-metal membranes have demonstrated exceptional durability in laboratory and field tests, exhibiting more than 150 days of continuous operation without flux decline or a decrease in the purity of the permeate  $\text{H}_2$ .

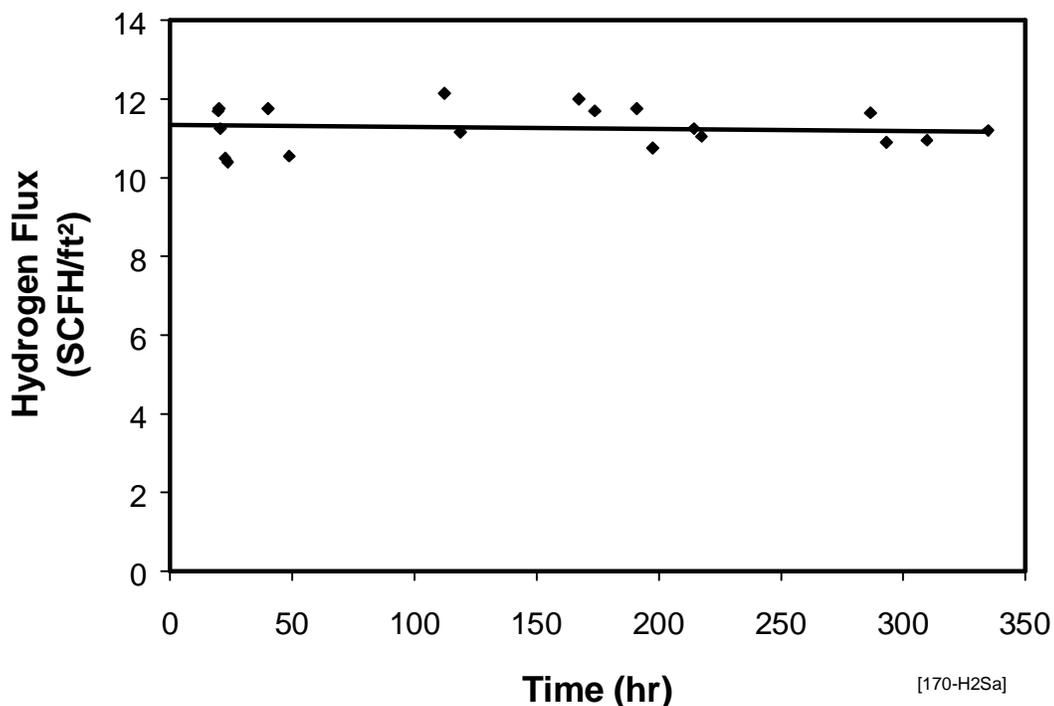


Figure 4. Long-Term Stability of H<sub>2</sub> Flux Through a 50- $\mu$ m-Thick Pd-40Cu Membrane  
Conditions: 500°C; feed is 1000 ppm H<sub>2</sub>S in H<sub>2</sub> at 100-psig total pressure;  
permeate is at ambient pressure

The durability and permeability of the Pd-40Cu membrane has been verified by independent tests conducted on a coal-gasifier slipstream by the University of North Dakota Energy and Environmental Research Center at Grand Forks, North Dakota (Swanson et al., 1996).

### Evaluation Of Corrosion-Resistant Alloys And Coatings For Reactor Construction

An important step in developing a practical and economical membrane for use in with feed streams containing H<sub>2</sub>S and other sulfur compounds is to identify suitable structural alloys for making the module components that will be in contact with the feed stream.

Acceptable materials for this purpose must satisfy two requirements:

- the alloy must exhibit a low rate of corrosion by hot H<sub>2</sub>S; and
- the alloy must have sufficient strength at high temperature to serve as a load-bearing component of the module.

We evaluated two classes of materials: (1) corrosion-resistant alloys with low iron content, and (2) aluminum-oxide-coated stainless steel prepared by a commercial process.

## **Corrosion-Resistant Alloys**

A search for alloys resistant to high-temperature corrosion by H<sub>2</sub>S revealed two promising candidates: (1) HR-160, a high chromium, low-iron stainless steel made by Haynes International, Inc. (Kokomo, Indiana); and (2) C103, an alloy containing primarily niobium and titanium made by Teledyne Wah Chang (Albany, Oregon).

These two alloys and a control sample of 316 stainless steel were tested for corrosion resistance with H<sub>2</sub>S at 700°C. These tests suggest that HR-60 will be unsuitable for use with hot H<sub>2</sub>S-bearing feed streams, but that C103 should exhibit adequate corrosion resistance and provide long operating lifetimes. C103 also has adequate strength at high temperatures for this application.

## **Aluminum-Oxide-Coated Stainless Steel**

The ALON Company (Tarrytown, New York) offers a commercial vapor-diffusion process for applying aluminum-oxide coatings to steel. This process, called Alonizing, initially produces an aluminum-rich coating on the steel that rapidly oxidizes in air, yielding a tenacious coating of aluminum oxide. Aluminum oxide has excellent chemical resistance to hot H<sub>2</sub>S, so we expected Alonized stainless steel to exhibit good stability to high concentrations of H<sub>2</sub>S at high temperatures. Samples of Alonized stainless-steel tubing were tested in 10% H<sub>2</sub>S in N<sub>2</sub> at 500°C to 700°C. These tests show that Alonized stainless steel exhibits good corrosion resistance to hot H<sub>2</sub>S. Structurally, alonized stainless steel is equivalent to the alloy from which it is prepared—these alloys have adequate strength at high temperature for this application.

## **Development Of New Reactor Designs**

We developed a plate-and-frame module that was successfully demonstrated as a membrane reactor for conducting equilibrium-limited reactions. Figure 5 shows the key elements of this reactor design. The various reactor components (end plates, feed plates, and ports for allowing sulfur-bearing gas streams to flow into and out of the reactor) can be fabricated from a corrosion-resistant alloy, such as C103, or fabricated from stainless steel and then coated with aluminum oxide using a process such as Alonizing.

We have focused our efforts on the plate-and-frame design due to its simplicity and durability. We have demonstrated that a catalyst bed can be incorporated into the membrane reactor at the feed side of the membrane (as shown in Figure 6). In another program, a prototype membrane reactor of this configuration has been used to drive an equilibrium-limited reaction toward complete conversion (Edlund et al., 1995)



## Evaluation Of Process Economics

Preliminary economic analyses indicate that the membrane-reactor process will ultimately be a cost-effective, energy-efficient, and environmentally acceptable means for the separation and treatment of H<sub>2</sub>S from hot coal-gasifier streams. We estimate that the proposed process will separate and decompose H<sub>2</sub>S at a cost that is one-half to one-fifth that of conventional technology for this application—amine scrubbers coupled with the Claus process.

## Potential Applications

The membrane-reactor process promises to offer an improved technology for H<sub>2</sub>S separation and treatment from hot coal-gas streams. By replacing expensive, complex conventional technology with a single, simpler technology, the proposed process would reduce the overall cost of coal gasification. This technology will help enable coal to become economically competitive with petroleum and natural-gas feedstocks for the manufacture of H<sub>2</sub> and syngas.

Two primary benefits would be realized through development of this technology:

- the efficient and economical separation and decomposition of H<sub>2</sub>S to environmentally benign products (hydrogen and sulfur) without the formation of sulfur oxides; and
- the reduction or elimination of Claus plants, a major source of sulfur oxide production and contributor to “acid rain.”

Successful development of the technology would also yield important secondary benefits, through increased use of coal as a feedstock. These benefits should include a decrease in reliance on foreign oil and an increase in the fraction of domestic oil and gas made available for transportation uses and production of clean-burning fuels.

In addition to the cleanup of hot coal gas, potential uses of the proposed membrane-reactor process include

- separation and recovery of H<sub>2</sub> from refinery gas streams that contain H<sub>2</sub>S; and
- decomposition of H<sub>2</sub>S to elemental sulfur and H<sub>2</sub> at refineries and natural-gas wells (in many cases replacing Claus plants and wet-oxidation processes for the treatment of H<sub>2</sub>S).

## Future Activities

Current development efforts are aimed at (1) improving the design of the membrane module to further reduce costs, and (2) continuing slipstream tests of the membrane module in feed streams that contain sulfur.

## Acknowledgements

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DE-FG03-91ER81228, titled "A Membrane Process for Hot-Gas Cleanup and Decomposition of H<sub>2</sub>S to Elemental Sulfur," METC Contracting Officer's Representative (COR): Thomas Dorchak; Period of Performance: 7/92 - 7/95 with extension; Subcontract Information: N/A.

DE-FG03-92ER81419, titled "A Process for Sweetening Sour Gas By Direct Thermolysis of Hydrogen Sulfide," METC Contracting Officer's Representative (COR): Venkat K. Venkataraman; Period of Performance: 5/93 - 5/95; Subcontract Information: N/A.

DE-FG03-91ER81229, titled "A Catalytic Membrane Reactor for Facilitating Water-Gas Shift Reaction at High Temperatures," METC Contracting Officer's Representative (COR): Venkat K. Venkataraman; Period of Performance: 3/92 to 3/95 with extension; Subcontract Information: N/A.

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